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A review of catalytic hydrogen production processes from biomass

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ABSTRACT

Hydrogen is believed to be critical for the energy and environmental sustainability. Hydrogen is a clean energy carrier which can be used for transportation and stationary power generation. However, hydrogen is not readily available in sufficient quantities and the production cost is still high for transportation purpose. The technical challenges to achieve a stable hydrogen economy include improving process efficiencies, lowering the cost of production and harnessing renewable sources for hydrogen production. Lignocellulosic biomass is one of the most abundant forms of renewable resource available. Currently there are not many commercial technologies able to produce hydrogen from biomass. This review focuses on the available technologies and recent developments in biomass conversion to hydrogen. Hydrogen production from biomass is discussed as a two stage process – in the first stage raw biomass is converted to hydrogen substrate in either gas, liquid or solid phase. In the second stage these substrates are catalytically converted to hydrogen.

Contents

1. Introduction

The inter-related problems of energy and environment are among the biggest challenges facing the world today, in particular energy sustainability and carbon emissions from the fossil fuels. Hydrogen has been projected as one of the few long-term sustainable clean energy carriers, emitting only water vapour as a by-product during the combustion or oxidation process. Although it is possible to use hydrogen as a fuel in internal combustion engines (ICE), its use in fuel cells, which act like batteries to convert chemical energy to produce electricity, is more attractive because of its higher efficiency [1]. The United States Department of Energy (DOE) launched an Energy Hydrogen Program in 2003 bringing together the offices of Energy Efficiency and Renewable Energy (EERE), Fossil Energy (FE), Nuclear Energy (NE), and Science (SC). Each office manages activities that address

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the hydrogen technologies which meet the needs of their respective feedstock and target applications. The Hydrogen Posture Plan, published by EERE in February 2004, envisaged a complete transition to a hydrogen economy by 2030–2040 [2]. It identifies various resources which can be utilised to produce hydrogen, including both renewable and non-renewable resources. An established technology, such as, steam reforming of methane or natural gas would be most likely adopted initially, because of its wide use and economic feasibility [3]. In the long term, the technology will evolve towards more renewable resources such as biomass or water electrolysis, greatly reducing NO_x and CO_x emissions.

There are several established and developing technologies to produce hydrogen from various sources. These technologies can be characterised in three categories, whereby hydrogen is produced with – (a) net positive emission of CO and CO_2, (b) CO_2 free emissions, and (c) CO_2 neutral emissions. Examples of type (a) include steam reforming, partial oxidation and autothermal reforming of hydrocarbons such as natural gas [4], as well as the shift reaction of gaseous products of coal gasification [5]. CO_2 free hydrogen production can be achieved through methane decomposition [6,7] and methane aromatisation [8,9]. However, hydrogen production can be environmentally friendly only if the resource used to extract hydrogen is carbon neutral. Resources like natural gas and coal require a lot of energy for mining and processing, adding to the CO_2 emissions during hydrogen production, thus increasing the environmental impact of hydrogen production from these sources. CO_2 neutral hydrogen production can be achieved by the conversion of biomass via gasification [10], pyrolysis of bio-oils [11], steam reforming of biomass derived higher alkanes and alcohols [4], and aqueous phase reforming of oxygenated hydrocarbons [12]. Biomass derived hydrogen can be classified as carbon neutral because the CO_2 released during hydrogen production is consumed by further biomass generation (neglecting the CO_2 produced from the fossil fuel energy required for operating the hydrogen production unit) [13]. In this manuscript we review the recent developments in the catalytic processes involved in hydrogen production from biomass, with particular attention given to the advances in the understanding of improvements in the catalyst properties.

Before the advent of the fossil fuel based economy in the 19th century, biomass was the major source of energy. However, the energy efficiency in the conversion of biomass was very low. Therefore, fossil fuel energy proved to be a more economical alternative for the developing society. With increasing industrialisation worldwide, energy demands have increased to a stage where fossil fuel energy will not be able to meet the sustained growth of the world economies in the near future. As a result, a major shift back towards a biomass based economy is required because biomass is one of the few current sustainable resources of renewable energy [14,15]. According to government estimates [16] of the current excess biomass resources (not including edible biomass) in the U.S., more than 50% of the domestic crude oil demands [17] can be met by biomass resources, based on the energy content of the dry lignocellulosic biomass [15]. The availability of excess biomass varies in other countries but is available in sufficient quantities in the major oil consuming countries to be economically viable for energy production. Therefore, this biomass based energy can be utilised to replace a major source of CO_2 emissions. Processes with high biomass-to-energy conversion efficiency are required to make this transition a reality and currently there are no obvious routes to achieve this. The leading research in this field is covered in this review with a focus on hydrogen production.

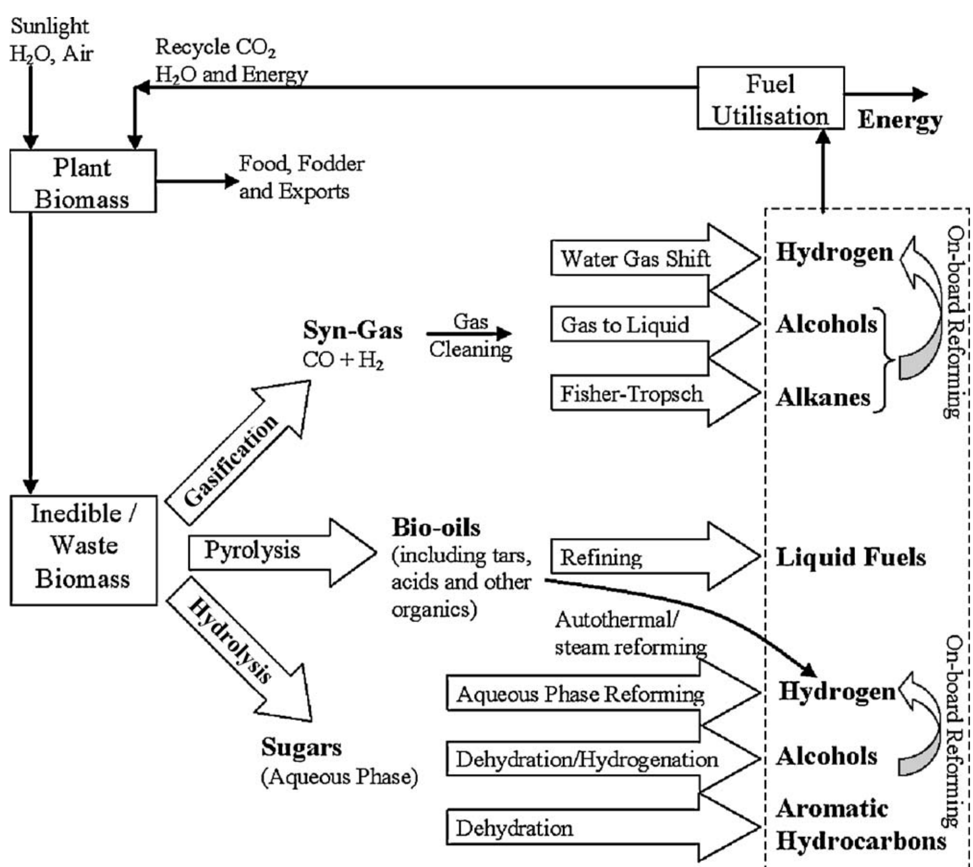


Fig. 1. Hydrogen and liquid fuels production from biomass sources. The waste CO_2, H_2O, and energy produced from these fuels can be utilised to produce further biomass. Adapted from Ref. [20].

2. Lignocellulosic biomass conversion

Lignocellulosic biomass (plant biomass) conversion can be achieved from various resources, including

1. Forestry wastes such as logging wastes, sawmill wood waste, and residues of the trees and shrubs.
2. Agricultural residues like animal and crop wastes (e.g. corn stover).
3. Energy crops like corn, sugarcane, grasses and aquatic plants like water hyacinth.

Residues of energy crops like corn stover and sugarcane or sorghum bagasse have high energy content per unit mass [18] and are therefore attractive for biomass conversion. Forestry residues of pine and eucalyptus have lesser heating value per unit mass and are costly to produce [18], but contain less ash content [19]. Lignocellulosic biomass, which represents the most abundant form of biomass, contains approximately 40–50% cellulose, 20–30% hemicellulose and 0–20% lignin [19].

Fig. 1 [20] illustrates the different routes which can be adopted to produce hydrogen from biomass, including gasification to produce syn-gas (Section 2.1), pyrolysis to produce bio-oils (Section 2.3) and hydrolysis of cellulose to produce sugar monomers (Section 2.5). Syn-gas can be converted to hydrogen by water gas shift (WGS) reaction (Section 2.2); however, any remaining CO must be removed from the gas stream. This can be achieved by preferential oxidation of CO. Pyrolysis bio-oil can be converted to liquid fuel but the processes are complex and the conversion is low. Hydrogen can be produced from the bio-oil by autothermal reforming (Section 2.4) with high conversion efficiency, especially with the use of catalytic membrane reactors. Aqueous phase reforming can be used to convert sugars and sugar alcohols, such as sorbitol, to produce hydrogen (Section 2.6). In addition to these, there are other biological (enzymatic and bacterial) routes to produce hydrogen, but the scope of this review is restricted to the heterogeneous catalytic routes only.

Hydrogen produced from biomass can be used as fuel in polymer electrolyte membrane (PEM) fuel cells to produce electricity for transportation purposes. In the short to medium term, this hydrogen can also be used for traditional purposes to minimise the environmental effects of the hydrogen derived from fossil fuels. Currently, industries produce approximately 50 M tonnes/year of hydrogen globally for ammonia synthesis, hydrogenation of crude oil to produce petrol and diesel and to hydrogenate edible oil. The benefits of a true hydrogen economy can only be achieved if the hydrogen is derived from renewable and carbon neutral resources like biomass [12].

2.1. Biomass gasification to produce syn-gas

Biomass gasification is similar to coal gasification, except that the biomass gasification is conducted at a much lower temperature. This is because biomass contains many more functionalities than coal and is therefore very reactive. Gasification is achieved at temperatures in excess of 700 °C in the presence of oxygen/air and/or steam, however tar free gasification requires much higher temperatures. Syn-gas (CO_2, CO, H_2) is produced when oxygen is used for the gasification as opposed to a producer gas (CO_2, CO, H_2, CH_4, N_2), in which case air is used for gasification. A combination of pyrolysis, partial oxidation and/or steam reforming of gaseous alkanes and char takes place under these conditions. Table 1 shows representative reactions which take place during gasification [15,21]. The presence of oxygen or air in the gasification equipment promotes partial oxidation over pyrolysis reactions. Although it is possible to obtain some gaseous products, as seen from Table 1, fast pyrolysis reactions generally produce bio-oils, tar and charcoal. Water gas shift reaction can be conducted in a separate reactor in the presence of CuO–ZnO or Fe catalyst depending upon the reaction temperatures (details of WGS in Section 2.2).

Catalytic cracking, gasifier type, design, heating rate, temperature and residence time can be optimised to maximise the efficiency of gasification with minimum tar formation. Tars are aromatic hydrocarbons which can be produced from the condensation of organic matter in the gasifier or further downstream [22], but it is generally formed in the gasifier at low operating temperatures. Thermal cracking of the tar is possible at temperature in excess of 1000 °C [22] and by using catalytic additives like dolomite, olivine and char [23], with 100% removal of tar reported by using dolomite as the gasifying agent [24]. Moreover, dolomite and CeO_2/SiO_2 supported Ni, Pt, Pd, Ru and alkaline metal oxides can be used to catalyse the gasification process to reduce tar formation and improve the product gas purity and conversion efficiency [25–27]. Although $Rh/CeO_2/SiO_2$ has been reported to be the most effective catalyst to reduce tar formation [26], Ni based catalysts are also highly active for tar destruction. Since Ni based catalysts are industrially used for steam reforming of methane and naphtha [28,29], they are also expected to catalyse the steam reforming of tars as well as WGS reaction to produce H_2. While alkali metal salts also decrease the tar yield, their use leads to an increase in char [27,30] and ash content, and are therefore not suitable for commercial use [31]. The inorganic contents of the biomass such as sodium, potassium, calcium and other alkali are converted to ash which is collected at the bottom of the gasifier or carried away with the product gas as fly ash [15,32]. Deposition of ash in the gasifier may cause sintering, fouling, agglomeration and slagging [33].

Recent improvements in the gasification technology include the Hydrogen Production by Reaction Integrated Novel Gasification

Table 1
Gasification reactions and enthalpies of selected C6 compound reactions. Adapted from Refs. [15,21].

Reaction type	Reaction equation		Enthalpy (kJ/gmol) at ref. temperature 27 °C and $x = 6$
Pyrolysis	$C_xH_yO_z \rightarrow (1-x)CO + (y/2)H_2 + C$	(1)	180
	$C_xH_yO_z \rightarrow (1-x)CO + ((y-4)/2)H_2 + CH_4$	(2)	300
Partial oxidation	$C_xH_yO_z + (1/2)O_2 \rightarrow xCO + (y/2)H_2$	(3)	71
	$C_xH_yO_z + O_2 \rightarrow (1-x)CO + CO_2 + (y/2)H_2$	(4)	−213
	$C_xH_yO_z + 2O_2 \rightarrow (x/2)CO + (x/2)CO_2 + (y/2)H_2$	(5)	−778
Steam reforming	$C_xH_yO_z + H_2O \rightarrow xCO + yH_2$	(6)	310
	$C_xH_yO_z + nH_2O \rightarrow aCO + (x-a)CO_2 + yH_2$	(7)	230
	$C_xH_yO_z + (2x-z)H_2O \rightarrow xCO_2 + (2n + (y/2) - z)H_2$	(8)	64
Water gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	(9)	−41
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	(10)	−206

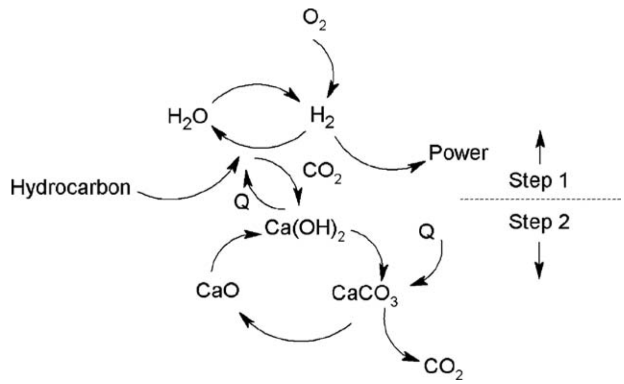


Fig. 2. Reaction mechanism in HyPr-RING gasification process. Adapted from Ref. [38].

(HyPr-RING) technology, first proposed by Lin et al. [5,34–38]. In this technology, the gasification and water gas shift reaction is combined in one reactor with simultaneous absorption of CO_2 and other pollutants to increase the hydrogen yield, while maintaining a relatively low reaction temperature of 650 °C. The reactions take place in a two-step process (Fig. 2) where in the first process water reacts with the hydrocarbon to produce H_2 and CO_2 (endothermic reaction). H_2 can then be used to generate power which produces water as the by-product. In the second step CO_2 is absorbed by $Ca(OH)_2$, which is in turn produced at high pressure by the hydration of CaO by water. The resultant $CaCO_3$ can be separated and regenerated to produce CaO and release pure CO_2 for sequestration. Although this technology was initially designed for coal gasification, we believe that important lessons learned from this technology can be applied to great effect in biomass gasification. With the high water content of the biomass, the gasification can proceed with little or no additional water supplied for the reaction.

One of the latest developments in gasification technology, called the Carbo-V process, has come from the CHOREN Technologies GmbH, formally called the Umwelt- und Energietechnik (UET) in Freiberg, Germany [39,40]. The main aim of this process is to produce tar free syn-gas for hydrogen or liquid fuel production. This process takes place in two steps. In the first step biomass is converted to tar containing gas and charcoal in a pyrolysis unit which operates at 500 °C. The tar containing gas is combusted in a high temperature gasifier by co-feeding oxygen. Here, the charcoal from the first reactor is completely gasified to syn-gas at 1500 °C in an entrained flow gasifier. The remaining ash is converted to slag which can be used as construction material because of its granular form. The advantages of Carbo-V process over the normal gasifier is that it increases efficiency (>80%) via – (1) chemical quenching by blowing charcoal into the hot gas, and (2) decreasing the heat losses in the combustion chamber because of indirect cooling. The low temperature pyrolysis reactor increases the feedstock flexibility as the solid feed is converted to combustible gas and charcoal.

A similar two-step process, called BIOLIQ, was developed at the Forschungszentrum Karlsruhe, Germany [41,42]. In this process, lignocellulosic biomass such as straw and other non-woody biomass is first liquefied by fast pyrolysis at many local small plants. The resulting bio-oil and char slurry is transported to a central facility where large pressurised entrained flow gasifiers combusts the slurry to produce tar free syn-gas. The gasifier is operated at 26 bar pressure and at temperatures ranging between 1200 and 1600 °C (typically above the ash melting point). Burners at the top of the gasifiers are fed by a nozzle that atomises the incoming slurry pneumatically by pure O_2 (at stoichiometric ratio of 0.3–0.7) at the gasifier pressure. The gasification takes place in a downward flame reaction in typically 1 s. The resulting syn-gas and molten ash exits the bottom of the gasifier into a quench zone where it is cooled by injecting water. High gasification efficiency (70% at 1200 °C operating temperature) and very high carbon conversion (>99%) have been reported with this process [42].

2.1.1. Biomass gasification in supercritical water

Gasification of biomass to produce syn-gas via the processes described so far is limited to biomass containing less than 35% water content [43]. In many cases however, the moisture content of available biomass may exceed that limit. In this scenario it is possible to gasify biomass under supercritical water conditions – water above its thermodynamic critical temperature (374.3 °C) and pressure (221.2 bar). After the pioneering work in supercritical water gasification (SCWG) carried out by Modell [44], several other researchers studied hydrolysis reactions of biomass products in near- or super-critical water [45–53] to produce various liquid products. At supercritical water temperatures in excess of 600 °C, hydrothermolysis of the biomass products will lead to gaseous products, including H_2, CO, CO_2 and CH_4, with 100% conversion [54–56]. This is a great advantage over conventional oxygen/steam gasification technology which leads to tar and char formation. SCWG can be categorised into two operating conditions based on their temperature. Low temperature SCWG is operated between 350 and 600 °C and high temperature SCWG is conducted at temperature in excess of 600 °C.

Low temperature SCWG was initially developed at Battelle Memorial Institute using a batch reactor [57,58] and was later adopted on a bench scale continuous reactor system [59]. As previously mentioned, 100% gasification is achieved only at temperatures in excess of 600 °C, therefore low temperature SWCG is performed in the presence of a catalyst. The catalysts used are generally composed of bimetallic Ru or Ni supported on titania, zirconia or carbon [60,61] which are stable under severe oxidising and corrosive conditions of the near-critical water. Use of homogeneous alkali solutions [62] and heterogenous alkali metal catalysts [63] have also been reported in SCWG, but recovery of such catalysts is a major problem. Reaction studies conducted by Minowa et al. without any catalyst [63–67] showed that the hydrolysis of cellulose to glucose was the primary step leading to various products depending upon the reaction temperature. At 200 °C, the hydrolysis resulted in mostly sugar formation with no oil, gas or char produced. At 250 °C, the products ranged from sugars to water-soluble non-sugar compounds including gas, oil and char. Finally, at temperatures in excess of 300 °C cellulose was completely decomposed to produce char as the main product, at 60% yield (on carbon basis) and 10% gas yield. Using sodium carbonate as a catalyst can reduce the onset temperature of cellulose decomposition, as well as, increase the gas and oil yield [63–67]. Metal catalysts like Ni did not reduce the onset temperature of the hydrolysis reaction but increased the yield of H_2 in the gas stream. After the hydrolysis of cellulose to produce sugars the Ni catalysed reaction proceeds similar to the steam reforming reaction, but in the liquid phase

$$C_6H_{12}O_6(l) + 6H_2O(l) \rightarrow 6CO_2(g) + 12H_2(g) \quad (11)$$

However, under these conditions the methanation reaction is also thermodynamically favourable and therefore some of the hydrogen evolved in Eq. (11) is consumed to form methane. Ni and many other metal catalysts also suffer from severe corrosion at supercritical water condition, especially at the high temperatures needed for higher H_2 yields. This problem was overcome by Antal and co-workers by using charcoal and other carbons as catalysts for the gasification of tars in supercritical water [56]. Carbon may seem to be an unlikely candidate for a catalyst at supercritical

water conditions, but the authors showed that in the presence of hydrogen and at the temperatures of supercritical water, carbon is very stable [68,69].

At high temperature SCWG conditions (600–800 °C) biomass is highly reactive, which increases the gasification efficiency but only at low concentrations. The gasification efficiency drops sharply with increasing feed concentration. To get around this problem researchers have conducted high temperature SCWG in two stages. The first stage involves hydrolysis of biomass to produce water-soluble compounds followed by gasification in the second stage [60]. Addition of alkali like KOH, $KHCO_3$ and Na_2CO_3 have been shown to increase the H_2 yield from the gasification of model biomass compounds such as glucose and pryrocatechol [62]. This may be due to the enhanced WGS reaction in the presence of an alkali [70]. To overcome the problem of high recovery costs of the alkali catalysts, zirconia can be used to catalyse high temperature SCWG reactions, however, the activity of zirconia is lower than Na_2CO_3 [71,72].

2.2. Hydrogen production from syn-gas

Relatively pure hydrogen can be obtained from syn-gas produced from the biomass gasification by steam reforming followed by a WGS reactor. During the WGS reaction, CO and H_2O react in a 1:1 molar ratio on a catalytically active metal site to form CO_2 and H_2 (Table 1). This is a reversible reaction and therefore steam is added in excess to shift the equilibrium towards the product side. The WGS reaction can be carried out at two temperature ranges – (1) the high temperature reaction is carried out using Fe and/or Cr based oxide catalysts at temperature between 350 and 500 °C, and (2) the low temperature reaction is carried out over Cu–Zn oxide catalysts [28] at 200–250 °C. Low temperature WGS reactions have also been carried out on metal catalysts supported on partially reducible metal oxides, such as transition metal catalysts [73] and Au [74] supported on Al_2O_3 [73,75], CeO_2 [75–77] and CeO_2–ZrO_2 [78]. CeO_2 is by far the most studied partially reducible support because of its ability to readily reduce from Ce^{4+} to Ce^{3+} over the temperature range where low temperature WGS reaction is favourable. Gold supported on ceria has shown great promise and has been reported to be stable up to 300 °C [79]. However, the higher temperatures upstream in a plant require more active and stable catalysts. Traditionally, high temperature shift catalysts based on oxides of Fe and Cr are used in the industry [80]. However, recently Trimm et al. reported that promotion of Fe_2O_3–Cr_2O_3 catalysts with small amounts of Rh can increase the activity by up to a factor of 4 [81,82]. The authors believed that the presence of Rh enhances the reduction of Fe_2O_3 to Fe_3O_4, and also increases the H_2 release rate during the reoxidation by water. Examples of Fe and Cr oxide catalysts promotion by Cu, Hg and Ag can also found in the in the literature [83,84]. Several other authors have studied the replacement or removal of chromium oxide from the catalyst due to the environmental restrictions on its disposal. These attempts include the substitution of Cr by Al [85] and promotion of Fe/Al catalyst by Co and Cu [86].

Zhang et al. illustrated a process they developed to produce hydrogen from switchgrass [87,88]. Fig. 3 illustrates schematically the processes involved in converting syn-gas to hydrogen on a pilot plant scale. The gasified biomass stream is filtered in a heated particulate filter and purified to remove tars in a guard bed dolomite reactor at 600 °C. The resulting syn-gas which may contain unreacted light hydrocarbons and traces of tar is converted to H_2 and CO by steam reforming reaction (Table 1) using a supported Ni catalyst at a temperature range of 750–850 °C. The remaining CO from the steam reforming reactor is converted by sequentially feeding the gas stream to a high temperature and low temperature water gas shift reactor to increase the H_2 yield. Steam reforming and shift reactors in coal gasification plants generally suffer catalyst deactivation due to sulphur poisoning; sulphur removal is therefore a necessary step prior to downstream processing. Since biomass contains very little sulphur, Zhang et al. did not attempt to removal the sulphur. However, they detected some sulphur and coke deposition which may cause catalyst deactivation in a long run.

2.2.1. H_2 purification by preferential CO oxidation

The CO concentration in the gas stream, as seen from Fig. 3, decreases to approximately 2% after the high temperature WGS reactor and finally reduced to less than 0.2% after the low temperature WGS reactor. However, CO is a poison for the anode catalyst used in the PEM fuel cells [89–91]. Therefore, generally it is expected that the CO concentration of the feed stream in the fuel cell is at sub-ppm level [92]. One of the ways to achieve this

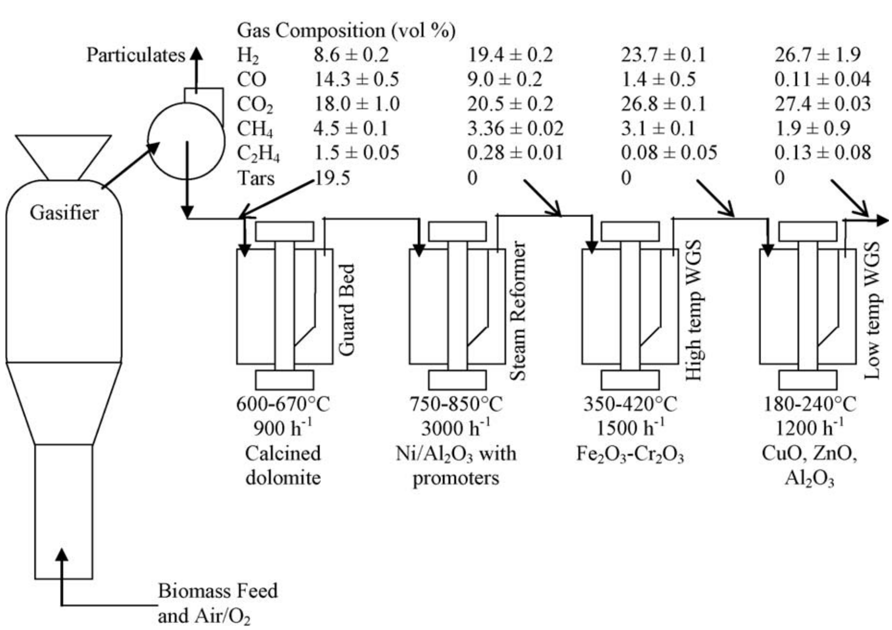


Fig. 3. Hydrogen production from syn-gas from biomass gasification. Adapted from Refs. [87,88].

economically is to preferentially oxidise CO (CO-PROX) [93,94]. Many researchers have reported CO-PROX in the H_2-rich stream using various catalysts based on Pt, Rh, Ru, Au and Cu–Zn, which can be supported on Al_2O_3, SiO_2, TiO_2, CeO_2, ZrO_2, MgO [95–103]. Promoting the noble metal catalysts with some additives have also been shown to enhance the catalytic performance for CO-PROX [101,104–106]. The use of alkali metals like Li, Na, K, Rb and Cs as additives was shown to be effective for increasing the catalytic performance, especially K–Pt/Al_2O_3, which proved to be one of the most active and selective catalysts [96,97,107–109]. Tanaka et al. studied the CO-PROX reaction in a H_2-rich stream with feed concentrations of 0.2–1% CO, 0.2–1.25% O_2 and 60–75% H_2, at temperatures ranging from 47 to 177 °C [96,97]. They found that the CO conversion increased with respect to temperature, and the highest conversion was achieved at temperatures in excess of 100 °C. The type and amount of alkali addition had a significant influence of the activity and selectivity of the catalysts used. The authors concluded that the addition of alkali metals decreased the CO adsorption strength on the active metal sites and also increased the metal crystallite size leading to the increased performance [96]. However, it is noteworthy that the presence of steam in the feed mixture inhibits the preferential oxidation reaction of CO by interacting with the active metal sites [97].

An interesting alternative to the CO-PROX is the use of a catalytic membrane reactor (CMR) for the WGS reaction for the conversion of syn-gas to H_2. There are two obvious advantages of using a CMR for the WGS reaction. First, the CMR shifts the equilibrium conversion of CO towards the products (CO_2 and H_2) by removal of H_2 from the reaction zone [110]. This also implies that compared to conventional reactors similar conversions can be achieved in a CMR at lower H_2O/CO ratios [111,112], thereby, reducing the cost of making the excess steam required for the WGS reaction. The second advantage of a CMR is that it can potentially eliminate the need for a traditional H_2 purification step (e.g. pressure swing adsorption), because the use of a highly H_2-selective, dense metal, diffusion membrane can result in H_2 recovery and purity in excess of 99% and 99.9999%, respectively [113]. A CMR can be prepared by using a fixed bed of catalysts inside a tubular membrane or by impregnating a film or nanoparticles of active metals on the inside wall of a tubular membrane or a combination of both [110–112]. The selection of the membrane material depends largely on its hydrothermal stability at the reaction conditions. Until recently the water gas shift CMR utilised Pd or Pd-alloy based dense metal membranes [114,115]. However, these catalytic membranes are susceptible to steam embitterment and catalyst poisoning [116]. Recent improvements in hydrothermal stability, H_2-selectivity and flux of silica membranes have created an interest in their use as CMR for the WGS reaction [116–118]. Despite these advances in the CMR technology in the last few years, they are still not commercially viable due to the high cost of membranes and the use of expensive Pd catalysts [119]. Durability of these membranes for a commercially acceptable lifespan is also in doubt at this stage.

An attractive alternative to the WGS reaction, proposed by Kim et al. [93,120,121], is the conversion of CO and H_2O to CO_2, H^+ and electricity. They carried out this experiment in an aqueous solution of polyoxometalates (POM) to achieve significantly higher rates than the WGS reaction. Eq. (12) illustrates the reaction of CO and water with POM, such as $H_3PMo_{12}O_{40}$, in presence of a gold catalyst:

$$CO + H_2O + 2PMo_{12}O_{40}{}^{3-} \xrightarrow{Au} CO_2 + 2H^+ + 2PMo_{12}O_{40}{}^{4-} \quad (12)$$

The aqueous solution of the reduced POM and protons can be used to produce electricity on the anode of a PEM fuel cell and thus the POM solution is reoxidised in the process.

2.3. Fast pyrolysis of biomass to produce bio-oils

Pyrolysis of biomass involves the thermal decomposition of the cellulosic matter in the absence of air or oxygen. Conventional carbonisation and pyrolysis has been used as a commercial process for many years to produce fuels (mainly charcoal), solvents and chemicals. This is a slow heating process, with temperatures ranging from 300 to 900 °C, which results mostly in charcoal formation. Therefore, this process is not attractive for producing hydrogen. In the early 1990s the fast pyrolysis technology was developed on a commercial scale and few pilot plant fluidised bed reactors were established in parts of US, Europe and Canada. Fast pyrolysis is characterised by fast heating rates, higher temperatures (400–3000 °C) and short residence times – generally in the order of fraction of a second [15]. A fast pyrolysis process leads to the formation of products in solid, liquid and gaseous forms depending upon the feed and temperature [122–124]. According to the recent reviews by Bridgwater and Peacocke [125] and Mohan et al. [126], high heating rates and fine particle size of biomass are required for fast pyrolysis leading to rapid heat transfer from the heat source. This initiates the primary pyrolysis reactions at elevated temperatures, releasing the volatiles and the remaining char. The hot volatiles may come in contact with cooler unpyrolised solids and condense, followed by secondary reactions to form tars [127]. To control the desired product range, accurate temperature control around 500 °C is essential. The completion of primary and secondary pyrolysis reactions results in organic vapours which are rapidly cooled outside the pyrolysis reactor to produce bio-oils with up to 80% yield on the dry biomass feed basis. The physical characteristics of bio-oil can vary considerably depending upon the feed type and the severity of pyrolysis. Typically bio-oils contain very high oxygen content (30–40%) and a lower heating value (16–19 MJ/kg) compared to heavy fuel oil (0.1% and 40 MJ/kg, respectively) [128]. Most of the oxygen is present as water content in the bio-oil (15–30%) and is also responsible for decreasing the heating value of the bio-oils. Furthermore, the high oxygen content also makes bio-oils chemically unstable, producing many unwanted chemical reactions with increasing time and temperature – leading to an increase in viscosity and the cloud point temperature. Other significant problems with bio-oils include poor volatility, high viscosity, coking, corrosiveness, and cold flow problems [128]. Therefore, refining of bio-oils is essential to make it suitable as a liquid fuel. However, distillation of bio-oils can lead to residual wastes of up to 50% by weight (compared to only 1% for heavy fuel oil).

An alternative to refining bio-oils is to increase the severity of pyrolysis conditions in order to produce more gases (CO, H_2, CO_2 and CH_4). The remaining bio-oil after condensation can then be treated further to produce additional H_2. Several researchers have worked on developing processes and catalysts to maximise hydrogen production from fast pyrolysis bio-oils [122–124,129–143]. Evans et al. [129] at the US National Renewable Energy Laboratory, proposed a scheme to produce H_2 and adhesives from pyrolysis bio-oils using some co-products. Fig. 4 illustrates a schematic diagram of this scheme using the fast pyrolysis of biomass to produce H_2 and chemicals [129,144]. Dried and finely ground biomass is fed into the pyrolysis reactor which produces char, organic vapours, and gases in varying concentrations depending upon the severity of pyrolysis. The chars can be centrifuged and utilised for heating purposes as illustrated in Fig. 4. The organic vapours can be condensed to produce bio-oils. H_2 yield can be subsequently increased from the gases coming out of the condenser using the processes described in Section 2.2. The bio-oils can then be separated into water-soluble and -insoluble components. The insoluble organics can be treated to produce

Table 2
Hydrogen yields and energy ratios obtained from various processes [124,142].

Processes	H_2 yield (wt%)	Energy ratio[a]
Pyrolysis + steam reforming	12.6	91
Gasification + WGS	11.5	83
Biomass + steam + except heat (theoretical maximum)	17.1	124

[a] Energy ratio = heating value of product H_2/heating value of the biomass feed.

chemicals and the soluble organics can be further steam reformed to produce H_2. Alternatively, all the bio-oil can be treated in an autothermal or steam reformer to produce H_2. Table 2 illustrates the H_2 yields that can be obtained from biomass using various processes and the theoretical maximum including the ratios of heating values of the product hydrogen with respect to the biomass feed [124,142].

2.4. Hydrogen production from fast pyrolysis and bio-oils

Gaseous products can be obtained from fast pyrolysis of biomass by increasing the pyrolysis temperature. Fig. 5 illustrates the effect of fast pyrolysis temperature on the yields of solids, liquids and gases produced from various feeds at different temperatures [142,145]. As the temperature increases from 500 to 750 °C, the char and liquids yields decrease while the gaseous yield increases. At 750 °C, the gaseous yield increases to around 45–50% compared to the yield of 30–35% at 500 °C, based on the dry biomass feed. Demirbas and Arin [123] also reported that increasing the pyrolysis temperature resulted in an increase in the H_2 yield as a percentage of the total gases evolved. Depending upon the feed, the H_2 yield increased from 27–41% to 41–55% of the total gas yield on a volumetric basis. Although these bench scale experiments show promising results, the H_2 yield is still too low for it to be commercially attractive. One of the methods to increase the H_2 yield is to apply catalytic pyrolysis. Chen et al. [145] studied the effect of catalysts on the pyrolysis reaction with mixed success. Ca and Cr oxides seem to perform the best in their studies. Garcia et al. [146] studied the effect of catalysts pre-treatment on the gaseous yield from the fast pyrolysis of sawdust. The pyrolysis was based on Waterloo Fast Pyrolysis Process (WFPP) technology [146]. This technology can achieve very fast heating rates and short residence time of the biomass (in the order of less than 1 s). The gas spatial time in the fluidised bed reactor is approximately 0.34 s at temperatures of 650–700 °C under nitrogen flow. A Ni/Al co-precipitated catalyst was used in this study to test the influence of calcination temperature (750–850 °C) and the activation condition (H_2 flow rate) on the gas yields. They reported an increase in H_2 and CO_2 yields when the catalysts were present in the reduced state. Moreover, reduction of the catalysts was achieved under the pyrolysis reaction condition when the catalysts were calcined at 750 °C. But catalysts calcined at 850 °C could not be reduced without the hydrogen pre-treatment.

Hydrogen can also be produced from the bio-oil products from the fast pyrolysis reactor using steam reforming which is similar to Eq. (8) in Table 1. Wang et al. [147,148] and Czernik et al. [133,141] have developed methods and catalysts for H_2 production from these bio-oils at the US National Renewable Energy Laboratory. Their initial studies were based on steam reforming of model compounds of oxygenated hydrocarbons, model bio-oils and the aqueous fraction of poplar bio-oil. During these initial studies they noticed that the steam reforming reaction competes with the gas-phase thermal decomposition reaction of the bio-oils. This may result in coke formation that can plug the reactor and deactivate the catalysts. Therefore, a special reactor design configuration

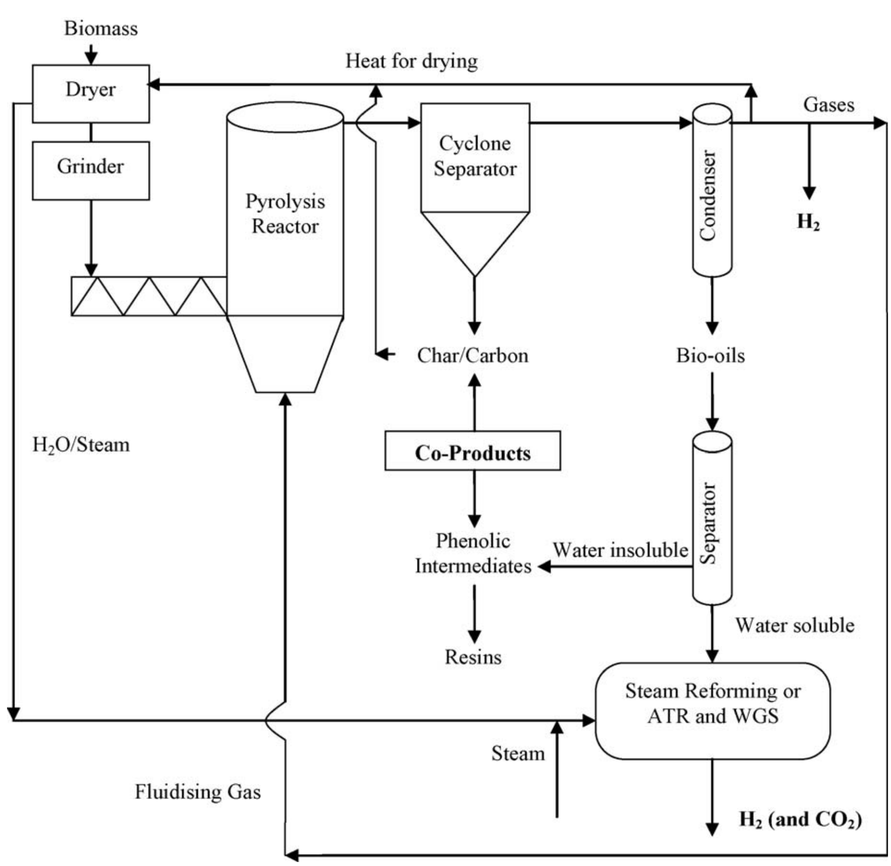


Fig. 4. Fast pyrolysis reactor system with integrated steam reforming or autothermal reforming (ATR) and WGS reactor to produce hydrogen and chemicals. Adapted from Refs. [129,144].

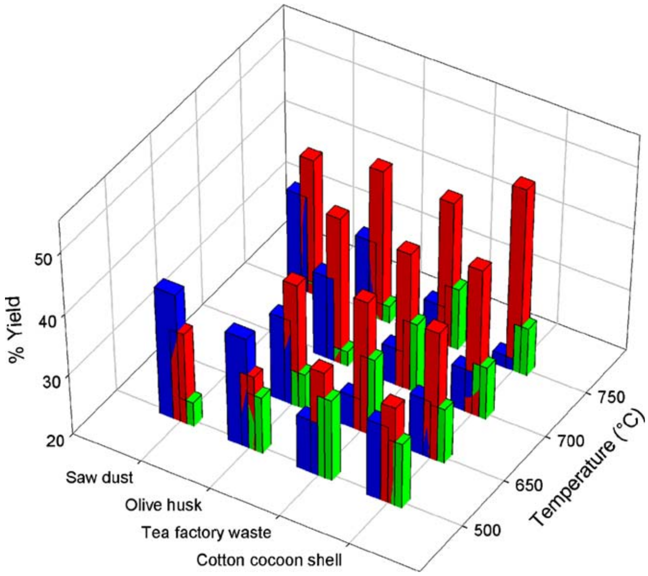


Fig. 5. Fast pyrolysis product yields – char (green), liquids (blue) and gases (red) obtained from various biomass samples. Data used from Refs. [142,145] (for saw dust data, liquids = tar + water). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

should be chosen to process the bio-oils and its fractions. A triple nozzle spray system was therefore used to introduce the bio-oils in the reactor which reduced the char formation from thermal decomposition. The H_2 yield (defined as the percentage of the stoichiometric maximum yield) from the aqueous fraction of poplar oil at 750 °C was found to be 75% at the start of the reaction, but decreased to ca. 60% over a 5-h period due to catalyst deactivation [147]. Catalyst regeneration conducted by passing steam at 800 °C for 12 h completely restored the catalyst. Another problem with steam reforming of the bio-oils is that a very high steam to carbon ratio is used to avoid coke deposition. In general steam to carbon ratio in excess of 7, at a space velocity of 1000 h^{-1}, is required to avoid a carbon deposit. This increases the energy demand of the plant in order to produce the excess steam.

Autothermal reforming (ATR) is an attractive alternative to steam reforming of bio-oils. ATR is a combination of steam reforming and partial oxidation of the hydrocarbons to produce CO, CO_2 and H_2. The reactions involved in the ATR include Eq. (8) (steam reforming) and the following:

$$C_xH_yO_z + \frac{x-z}{2}2O_2 \rightarrow xCO + \frac{y}{2}H_2 \quad (13)$$

$$C_xH_yO_z + \frac{(x-z+y/2)}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2O \quad (14)$$

$$C_xH_yO_z + \frac{(2x-z+y/2)}{2}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad (15)$$

The overall reaction for ATR can therefore be written as [149]

$$C_xH_yO_z + aO_2 + bH_2O \leftrightarrow cCO + dH_2 + eCO_2 \quad (16)$$

This is a simplified reaction and the coefficients *a–e* will depend on the reaction temperature and the amount of disposable hydrocarbon [130]. One of the advantages of ATR over steam reforming is that the heat generated from the exothermic oxidation/partial oxidation of bio-oils can be provided to the endothermic reforming reaction. The other advantage is that the water produced as a by-product of Eqs. (14) and (15) can be utilised during steam reforming (Eq. (8)) which reduces the external water and energy required for producing excess steam. The oxygen concentration in the feed can be adjusted to match the heat required for steam reforming only, or for preheating and steam reforming. A thermodynamic study of autothermal reforming of model bio-oil compounds such as acetic acid, ethylene glycol and acetone showed that at temperatures in excess of 600 °C and O_2/feed molar ratio >0.3–0.5, H_2 yields comparable to that of steam reforming can be produced [130]. The optimum reaction conditions and the autothermal reforming yields are given in Table 3 [130], which shows that the steam to carbon ratio is reduced to 3:1 compared to >7 required for the steam reforming reaction. The H_2 yield from these model compounds was found to be 71–78% of the stoichiometric yield, which is comparable to the steam reforming reaction yields of approximately 80% reported in the literature [133,141,147].

Very recently, H_2 has also been produced from bio-oils using the sequential cracking method [134,135]. Bio-oil sequential cracking is a two step process in which catalytic cracking of feed is alternated with a catalyst regeneration step. This process is similar to methane sequential cracking [150–152] given by the following equations:

$$CH_4 + \xrightarrow{metal} C_{metal} + 2H_2 \quad (17)$$

$$C_{metal} + O_2 \rightarrow CO_2 \quad (18)$$

During the cracking step (Eq. (17)) the hydrocarbon feed decomposes on a metal catalyst surface to produce H_2 and solid carbon on the metal site which accumulates as coke. During the regeneration step (Eq. (18)) the coke deposited on the metal site is combusted or gasified to produce CO_2 and this restores the catalytic activity in the process. If two or more reactors are placed in parallel, H_2 can be produced continuously by cyclically switching the hydrocarbon and O_2 feed between the reactors. This process has an added advantage in that the H_2 and CO_2 are produced in different steps, thereby, saving the energy required to purify H_2. Platinum group metals supported on Al_2O_3, ZrO_2, and CeO_2–ZrO_2 have been used for this process [134,135].

2.5. Hydrolysis of biomass to produce sugars

Biomass hydrolysis technology to produce sugar monomers include dilute acid hydrolysis [153–155], concentrated acid hydrolysis [156], alkaline hydrolysis [155], enzyme hydrolysis [157,158] and near- and super-critical water hydrolysis. Near- and super-critical water hydrolysis was discussed in Section 2.1 as an intermediary of the SCWG process. Yu et al. [159] also recently conducted a review of biomass hydrolysis in hot

Table 3
Optimum reaction parameters and yields, as determined by a thermodynamic study of autothermal reforming of model bio-oil compounds. Adapted from Ref. [130].

Reaction parameters	Acetic acid	Acetone	Ethylene glycol
Steam/carbon ratio	3/1	3/1	3/1
O_2/feed ratio	0.33	0.62	0.26
Reaction temperature (°C)	627	627	627
Reaction pressure (atm)	1	1	1
Conversion (%)	100	100	100
Yield % (based on carbon except for H_2)			
H_2 (based on stoichiometric H_2)	72.59	70.97	77.40
CO	19.74	27.80	24.46
CO_2	79.69	70.13	74.07
CH_4	0.58	2.07	1.47

compressed water. Moreover, since the scope of this review does not including biochemical process we will not discuss the enzyme hydrolysis process. In this section we discuss only the dilute/concentrated acid and alkaline hydrolysis in detail. Briefly, the mechanism of hydrothermal hydrolysis of cellulose involves cleavage of a C–O–C bond by a water molecule, as shown in Fig. 6 (pathway C) and the subsequent formation of glucose monomers. During the hydrothermal treatment organic acids like acetic acid and formic acid are also formed, shifting the pH from neutral (or just below) to approximately 3 [155]. The reaction rate constant is however independent of the pH of the solution. The reaction follows a first order mechanism up to the transformation yield of over 90%. Conversion of cellulose with respect to time is strongly dependent on the reaction temperature and the activation energy is calculated to be 136 kJ/mol [155]. This activation energy is slightly higher than that for acid hydrolysis but is within the range of various acid catalyst experiments. One of the interesting aspects to note here is that the maximum glucose yield from hydrothermal hydrolysis is approximately 60% because of the conversion of glucose into further degradation products. The complete mechanism is defined in Fig. 7, where A′ is the intermediate product.

2.5.1. Acid hydrolysis

Acid hydrolysis of cellulose, shown in Fig. 6 (pathway A), involves the C–O–C bond cleavage by protonation of the glucoside bonds. In the first step, the proton (H^+) may attack either the oxygen bond between the two glucose units (pathway A_1) or the cyclic oxygen bond in the glucose unit (pathway A_2) [160]. The conjugated acid intermediates are believed to be formed rapidly followed by a slow reaction step involving splitting of glucosidic bonds by the addition of a water molecule and releasing a proton. Apart from the hydrolysis reaction pathways illustrated in Fig. 7 cellulose may be modified to form unreactive compounds, which do not go through the hydrolysis reaction to produce sugars [161]. The rate constants of hydrolysis reaction are directly correlated to the proton concentration in the reaction. Therefore, the strength of the acids used for hydrolysis is an important parameter in determining the effectiveness in the cleavage reaction. Effectiveness of the acids for the cleavage decreases in the order of their pK_a (acid strength) value – $HCl > H_2SO_4 > HNO_3 > CF_3COOH > H_3PO_4 > HCOOH > CH_3COOH$ [155]. For mineral acids the hydrolytic activity, defined by their pH value, can be increased with an increase in reaction temperature. However, the organic acid activity decreases with increased temperature. Therefore, a high

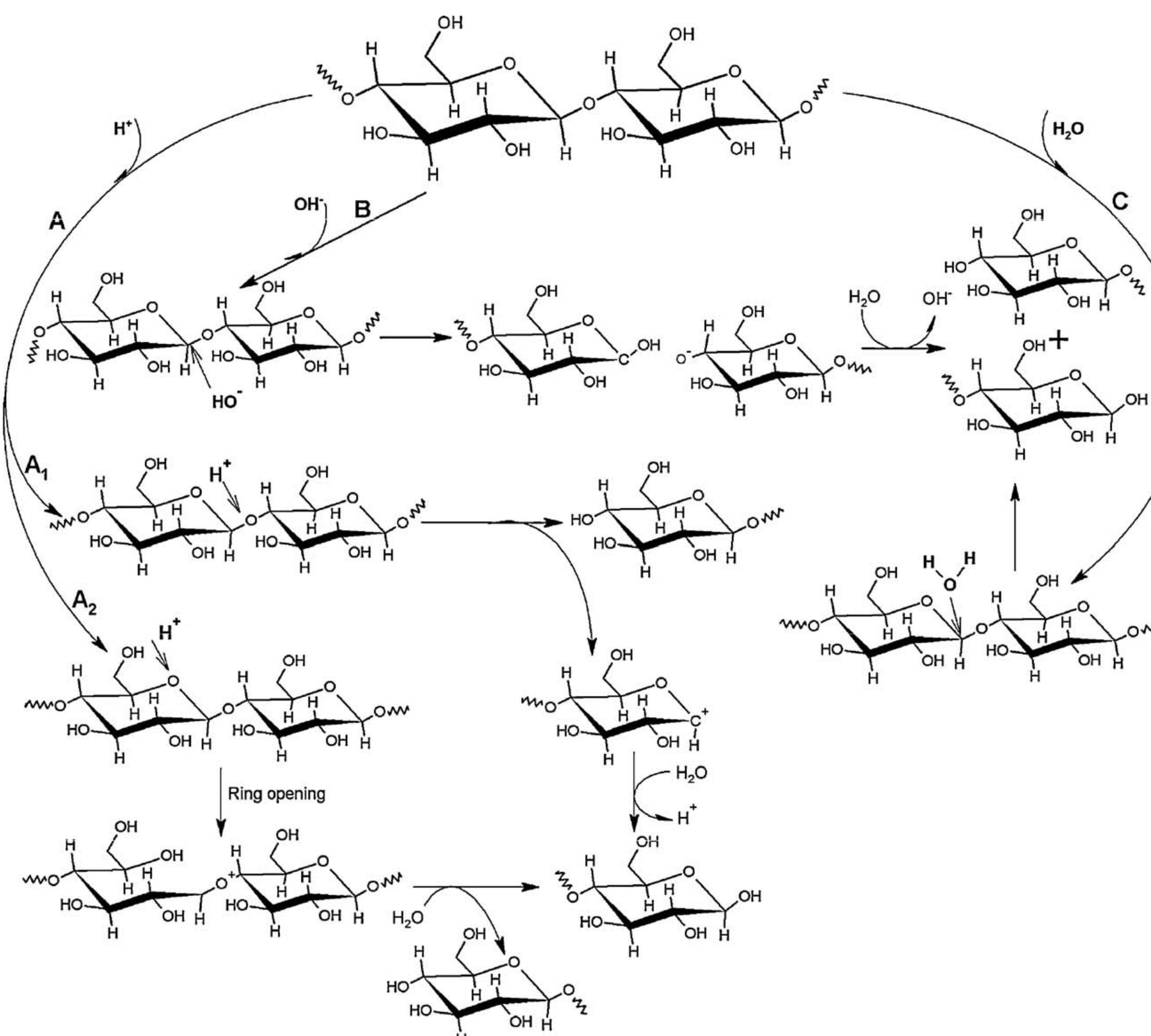


Fig. 6. Mechanisms of hydrolysis of cellulose in acidic (H^+), alkaline (OH^-), and hydrothermal media (H_2O). Adapted from Bobleter and Fan et al. [156,160].

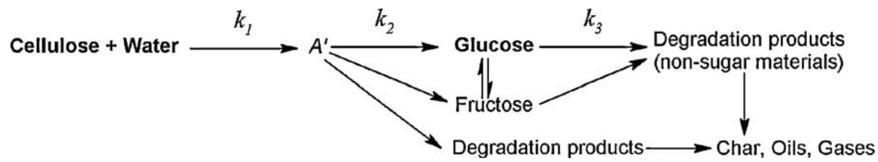


Fig. 7. Reaction scheme of cellulose hydrothermal hydrolysis. Adapted from Refs. [155,159].

concentration (>50%) of organic acids, like acetic acid, at moderate temperatures (160–185 °C) can be used to achieve high activity.

Dilute acid hydrolysis is carried out at high temperatures and pressures with reaction time in the order of a few minutes. This is suitable for a continuous process on a commercial scale application as it is possible to achieve a glucose yield of up to 50% using dilute acid hydrolysis [156]. Higher glucose yields can be achieved with shorter reaction time to avoid further degradation, but higher temperatures are required for that, which creates a problem of low thermal efficiency due to the heat-transfer limitation. Counter-current continual shrinking bed reactor technologies have been successfully employed to achieve glucose yield in excess of 90% from cellulose hydrolysis [162,163]. Unlike traditional fixed volume reactors, a continual shrinking bed reactor has a spring that maintains a tight and uniform packed bed of biomass solids, thus forcing the hydrolysis medium close to the solid surface. Torget and Lee proposed that to achieve the high yield of glucose from crystalline cellulose, a 'scouring' of the solid phase by the liquor phase is necessary [153].

Another method to maximise the glucose yield from dilute acid hydrolysis of cellulose is to carry out the reactions in two stages. The first stage involves dilute acid treatment under mild conditions (temperature and pressure) and short residence time (few minutes). This step decreases the degree of polymerisation of cellulose to form oligomers and C5 sugars. The C5 sugars are recovered at this stage and the second stage is optimised to recover C6 sugars. The second step is conducted at higher temperature, and acid concentration, and longer residence time (1.5–3 h) [162–164].

Concentrated acid hydrolysis uses highly concentrated sulphuric acid to convert the crystalline cellulose into an amorphous form. Sulphuric acid breaks the hydrogen bonds between the cellulose chains and the resulting amorphous cellulose forms a homogeneous gel in the acid solution. In the amorphous form cellulose is easy to hydrolyse in water at low temperatures, providing a rapid and complete conversion to glucose [159,165]. However the process faces many challenges for commercialisation because of the highly corrosive acid environment and high costs of acid consumption and recovery.

2.5.2. Alkaline hydrolysis

In alkaline hydrolysis, shown in Fig. 6 (pathway B), OH^- ions attack the anomeric carbon atom, thereby, cleaving the C–O–C bond. With the addition of a water molecule and the release of an OH^- ion in the next step, the glucose monomer units are formed. Experimental results suggest that the rate of alkaline hydrolysis of cellobiose (the basic repeating unit in cellulose) and water-soluble carbohydrates is higher than that of acid hydrolysis and hydrothermal hydrolysis [155,159]. However, the sugar monomers and dimers are severely attacked in alkali solutions, leading to degradation such as tautomerism of aldose and ketose with enediols [166]. Alkali degradation of dilute solutions results in near 100% conversion of sugar monomers into <C6 acids. Moreover, the composition of reaction products is independent of reaction temperature [166]. Hemicellulose is relatively stable to the alkali treatment but starts degrading at temperatures greater than 100 °C. Cellulose is stable to alkali treatment at temperatures below 170 °C [166] and is known to increase in crystallinity and the glazed appearance after 1 h treatment with 18% NaOH solution at 100 °C [167]. However, cellulose can be depolymerised in boiling diluted NaOH solution at temperatures ≤170 °C [166]. This is caused by the dissolution of short-chain molecules at the reducing ends of the cellulose chain (known as peeling) [168]. When cellulose is treated at more than 170 °C in an alkali solution random cleavage of glucosidic bonds results in rapid decrease in the degree of polymerisation [169]. At this point, apart from the monomer degradation, the alkaline hydrolysis also suffers from the formation of organic acids such as isosaccharinic acid, lactic acid, etc. This decreases the pH of the reaction and makes it difficult to determine the reaction parameters. Therefore, alkali treatment may only be used as a pre-treatment of lignocellulosic biomass before enzymatic hydrolysis. Low alkali concentration (e.g. 1% NaOH solution) at room temperature can considerably enhance the efficiency of enzymatic hydrolysis using cellulose [155]. Table 4 presents the summary of all the hydrolysis methods discussed in this section, including the advantages and disadvantages of each method [155,170].

Table 4
Summary of the reaction parameters, glucose yield (from cellulose hydrolysis), advantages and disadvantages of various hydrolysis methods. Adapted from Yu et al. [159] using data from Refs. [155,170].

Hydrolysis method	Reaction parameters	Glucose yield (%)	Advantages	Disadvantages
Hot compressed water	150–250 °C 100–250 bar 0–20 min	<40	Environmentally friendly Low maintenance cost High reaction rate	Lower sugar yield compared to other methods
Concentrated acid	30–70% H_2SO_4 40 °C 2–6 h	90	High sugar yield/recovery High reaction rate	Corrosion Environmental issues High recovery costs
Dilute acid	<1% H_2SO_4 215 °C 3 min	50–60	High sugar yield/recovery Very high reaction rate	Corrosion Environmental issues Sugar degradation High operating and utility costs
Alkaline	18% NaOH 100 °C 1 h	30	High reaction rate	Low sugar yield Acid formation during reaction lowers pH Sugar degradation

2.6. Hydrogen production from aqueous phase reforming

Initially Antal et al. [171] proposed the use of glucose as potential feedstock for hydrogen production via the steam reforming reaction. However, this reaction resulted in the formation of a hydrocarbon-rich syn-gas, with low hydrogen yields. Recently, a new method involving the oxygenated hydrocarbon decomposition was developed by Dumesic and co-workers [12,20,172–182]. They were able to convert biomass-derived oxygenated hydrocarbons with C:O ratio of 1:1, such as methanol, ethylene glycol, glycerol, glucose and sorbitol, into H_2, CO, CO_2 and gaseous alkanes by the catalytic aqueous phase reforming (APR) reaction using supported metal catalysts. The APR is carried out at a temperature range of 200–250 °C and pressures of 10–50 bar to maintain the liquid phase. The advantages of this method include moderate reaction temperature and pressure which favours the WGS reaction in the same reactor, low CO level in the gas stream (100–1000 ppm), which is ideal for fuel cell application and a lower energy requirement compared to steam reforming because the oxygenated hydrocarbon feed and water are in the liquid phase. Additionally, the feedstock is non-hazardous which makes its storage relatively easier.

The overall reaction for hydrogen production from oxygenated hydrocarbon with C:O = 1:1 by APR, shown in Eq. (19) is similar to the steam reforming reaction (Eq. (8)):

$$C_xH_{2x+2}O_x + xH_2O \rightarrow (2x+1)H_2 + xCO_2 \quad (19)$$

Although this reaction is thermodynamically favourable for the production of H_2 and CO_2, in these conditions the products can further react to form alkanes and water:

$$CO_2 + 4H_2O \leftrightarrow CH_4 + 2H_2O \quad (20)$$

Fig. 8 shows the reaction pathways involved in the formation of hydrogen, CO, CO_2 and alkanes. One of the pathways, similar to the steam reforming reaction (Eq. (8)) is to produce adsorbed CO on the metal site by the C–C bond cleavage. It is followed by the WGS reaction (Eq. (9)) to produce H_2 and CO_2. The combined reaction is given by Eq. (19). However, the Fischer–Tropsch reaction [183,184] to form alkanes and water presents a series selectivity problem because it consumes hydrogen. A parallel reaction proceeds through the cleavage of C–O bonds to form alcohols. Other pathways involve dehydration/hydrogenation and dehydrogenation/rearrangement of the oxygenated hydrocarbons to form alcohols and acids, which reacts with water to give alkanes, H_2 and CO_2. These reaction pathways present a parallel selectivity challenge which should be overcome to maximise the hydrogen yield.

The optimum catalytic pathway for the production of H_2 and CO_2 by APR of oxygenated hydrocarbons involves cleavage of C–C bonds as well as C–H and/or O–H bonds to form adsorbed species on the catalyst surface [184]. Therefore, a good catalyst for production of H_2 by aqueous phase reforming must be highly selective for C–C bond cleavage and promote removal of adsorbed CO species by the WGS reaction. However the catalyst must not catalyse C–O bond cleavage and hydrogenation of CO and CO_2. Cleavage of C–C bonds can occur over Pt, Pd, Rh, Sn, Ni, Co, Cu, Zn and their combinations [178]. Davda et al. reported that on silica support the activity for APR, measured by the rate of CO_2 production per catalytic metal surface site at 210 °C, decreased in the following order – $Pt \sim Ni > Ru > Rh \sim Pd > Ir$ [178]. Although the activity of Ni is comparable to that of Pt catalyst, its H_2-selectivity and stability is very low. Ni/SiO_2 showed significant deactivation at 225 °C, making it unsuitable for long runs. Pt and Pd based catalysts exhibit low selectivity for C–O bond cleavage and the series reactions, namely the methanation and Fisher–Tropsch reactions. Pt was found to be the most suitable catalyst for the APR reactions but the cost of this catalyst is prohibitive for large-scale applications.

The activity and selectivity of the metal catalysts also depends on the supports used. In general, acidic supports such as SiO_2–Al_2O_3 are more alkane-selective and the basic/neutral supports such as Al_2O_3 and carbon are more H_2-selective. pH of the solution should also be neutral for higher H_2-selectivity. This can also be seen from Fig. 8, where dehydrogenation of the feed leads to acid formation, reducing the pH and leading to the production of more alkanes. H_2-selectivity also decreases with increasing number of carbon atoms in the feed molecule. The H_2-selectivity decreases in the following order: methanol > ethylene glycol > glycerglycerol > sorbitol > glucose [12]. The H_2-selectivity of catalysts can be improved by alloying Pt and Pd with Ni, Co and Fe supported on high selectivity supports such as Al_2O_3. PtNi and PtCo catalysts with atomic ratios from 1:1 to 1:9 have been shown to improve the selectivity of ethylene glycol reforming [172].

2.6.1. Hydrogen production from sugars

We reported previously that hydrogen can be produced from APR of sugars and sugar alcohols [181,185–188]. Sugars and sugar alcohols, like sorbitol, can be directly produced from hydrolysis of biomass [155,159,189]. However, sugar reforming presents a greater challenge than methanol and ethylene glycol reforming because of the more complex chemical structure of sugars, which results in parallel selectivity issues [187]. Initial tests were carried out in a batch reactor for reforming of aqueous solutions of glucose, fructose and sucrose [185]. Fig. 9 shows the possible routes of reaction for APR of fructose using Pt/Al_2O_3 catalyst at 200 °C. Initially, the fructose molecule goes through dehydrogenation process selectively on the metal surface to give hydrogen and adsorbed organic species on metal site. According to density function theory studies of Gursahani et al. [190] C–C bonds are selectively adsorbed on the platinum site at temperatures around 200 °C. The adsorption of C–C bond results in cleavage and formation of CH–OH group adsorbed on metal (* representing the metal site). CH–OH then dehydrogenates to produce CO and hydrogen. CO might then go through WGS reaction to give CO_2 and H_2 or it might go through methanation reaction to give CH_4 and water. It is clear that the hydrogen consuming reactions are unwanted and therefore the catalysts must be WGS selective. Fig. 9 also shows that the adsorbed fructose molecule might then go through further C–C cleavage to give acetic acid and adsorbed CH–OH, which is again a desirable reaction as it results in higher hydrogen selectivity. It is known from the literature [182] that C–C bond cleavage is the limiting factor in the reforming process. In the lack of active metal sites, as was the case with alumina only study, the dehydrogenation of the fructose molecule does not produce C–C cleavage [187]. Presence of ketones and esters were detected in this case which might be the result of C–O bond cleavage followed by dehydration. This reaction takes place on weak acid sites of γ-Al_2O_3 [191]. The formation of these organic groups results in lower selectivity of hydrogen as they do not take part in further reforming reactions.

APR of sorbitol is more selective for hydrogen production compared to sugars because of the lack of an ester group. We studied the APR of sorbitol using alloy catalysts of Pt, Ni and Pd. We found that alumina nanofibre (Alnf) supported Ni–Pt catalyst in an atomic ratio of 33:1 was the most active and selective catalyst for APR of sorbitol [181,188]. Characterisation of the mono- and bimetallic catalysts of Ni, Pt and Pd showed that alloying Ni with noble metals results in a higher number of active sites due to the increased reducibility. Moreover, the alloy catalysts showed lower CO-chemisorption binding strength compared to its constituent monometallic catalysts. The differential heat of CO-chemisorption,

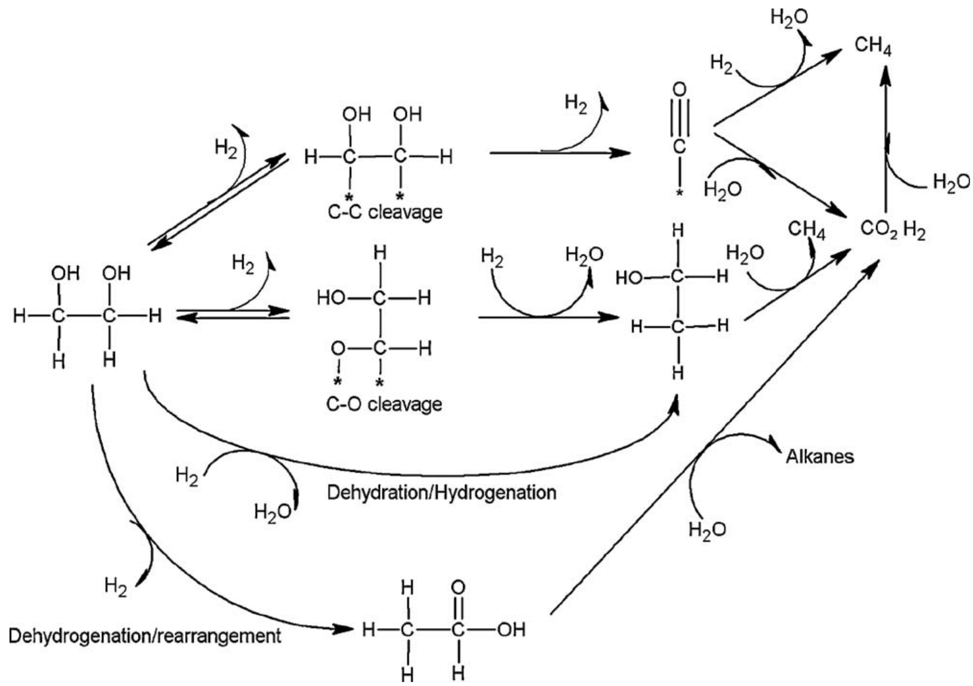


Fig. 8. Reaction pathways for ethylene glycol reforming during aqueous phase reforming. Adapted from Refs. [12,182]. The asterisk symbol (*) denotes the adsorption site on the metal surface. C–C cleavage followed by WGS is the desired pathway whereas the C–O cleavage, dehydration/hydrogenation and dehydrogenation/rearrangement reactions create parallel selectivity issues.

measured by a heat-flux calorimeter, was found to be 111.28 kJ/mol for Ni–Pt/Alnf, which was 11.45 and 5.51 kJ/mol lower than Pt/Alnf and Ni/Alnf, respectively [181]. The decrease in CO binding strength results in removal of adsorbed CO species by WGS reaction (Fig. 8) and therefore a higher fraction of active metal sites is available for the reforming reaction. The turn over frequency (TOF) of H_2 production, defined as moles of H_2 per mol of surface site measured by CO chemisorption, was found to be maximum for Ni–Pt/Alnf, which was 2 and 5 times more than Pt/Alnf and Ni/Alnf, respectively. The TOF of H_2 production from APR of 10 wt% sorbitol solution at 200 °C, 20 bar and WHSV = 6.2 h^{-1} using Ni–Pt/Alnf catalyst was found to be 0.074 min^{-1} at 62.5% sorbitol conversion and 75.6% H_2-selectivity [181]. This rate of formation compares favourably with the results reported by Cortright et al. [12] where they achieved H_2 TOF = 1.0 min^{-1} at 225 °C using 3% Pt/Al_2O_3, but at lower conversion rates. According to Cortright et al. [12] the TOF drops sharply with increase in conversion rate – e.g. the H_2 TOF from APR of ethylene glycol was reported to decreases from 7 min^{-1} at 3.5% conversion to 0.7 min^{-1} and 0.08 min^{-1} at 62% and 90% conversion, respectively.

Davda et al. [173] investigated hydrogenation of glucose to form sorbitol, followed by APR in a hydrogen-rich environment to produce H_2. The hydrogenation of glucose takes place on metal catalysts with high selectivity at low temperature (e.g. 125 °C) and high H_2 pressure (50 bar). However, the APR is H_2-selective at pressures just above the bubble-point pressure of the liquid feed

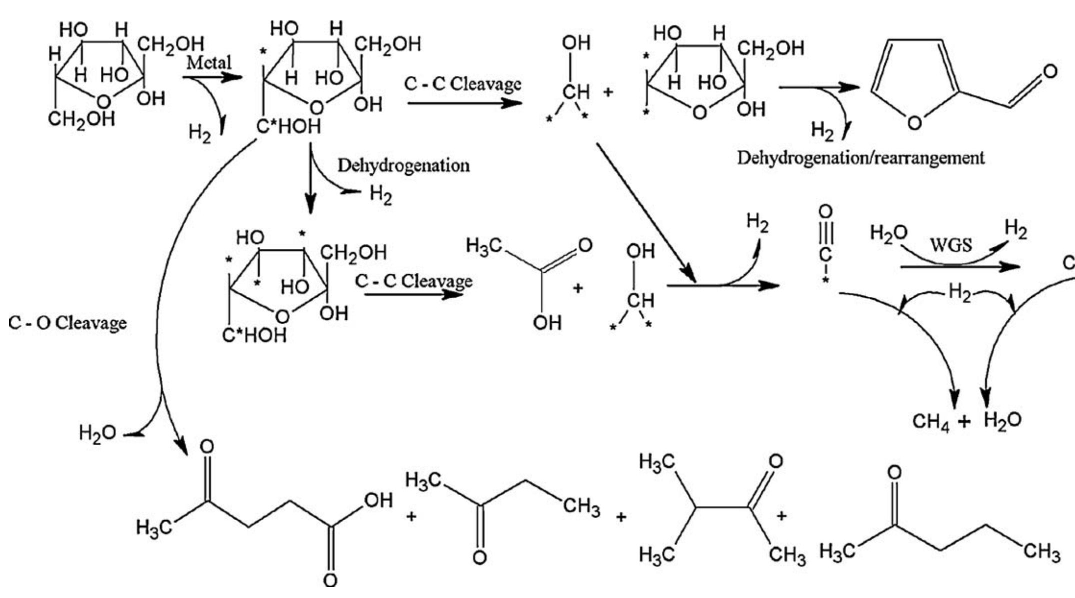


Fig. 9. Reaction mechanism of fructose reforming. Adapted from Ref. [187].

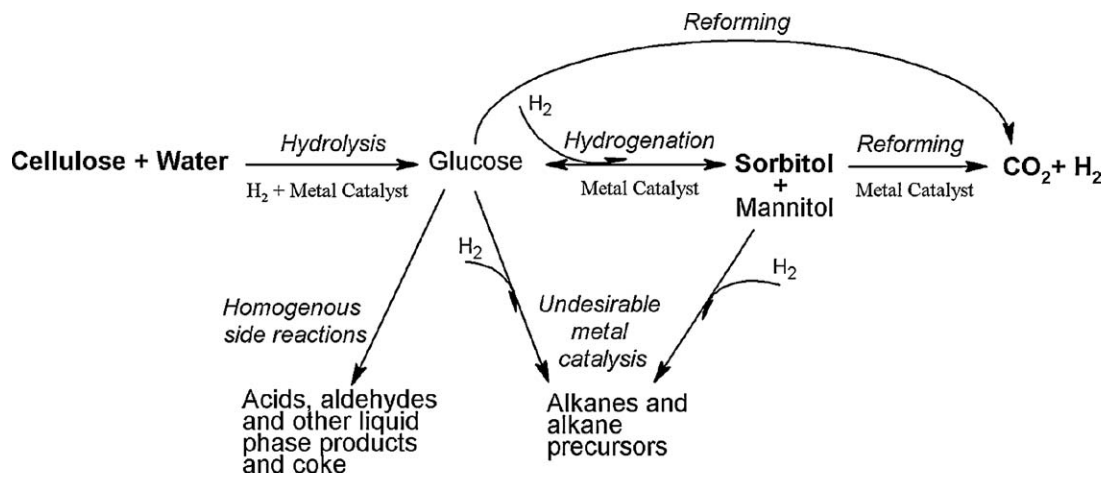


Fig. 10. Reaction pathways involved in APR of glucose and sorbitol produced from cellulose hydrolysis over metal catalysts. Adapted from Refs. [175,189].

Table 5
Summary of the hydrogen production processes from biomass including process energy ratios and advantages and challenges facing these processes.

Biomass conversion processes	Products	Hydrogen production processes	Energy ratio[a]	Advantages (A), challenges (C)
Gasification	Methane	Steam reforming	36–73% [21,192]	A: commercially available technology; high conversion of biomass to syn-gas
	Syn-gas	Water gas shift		C: increasing the low energy ratio
	Tar	Preferential CO oxidation		
		Thermochemical cracking		
Fast pyrolysis	Gases (CO, CO_2, H_2, CH_4)	Autothermal/steam reforming	60–90% [21,124,142]	A: high energy ratio; fast pyrolysis is commercially available technology
	Bio-oil	Sequential cracking		C: catalytic challenges for increasing the efficiency of bio-oil conversion; commercialisation of bio-oils to hydrogen technologies
	Char	Water gas shift		
Hydrolysis	Sugar monomers (C_5–C_6)	Aqueous phase reforming	20–45%[b]	A: high conversion of cellulose to sugars using enzymatic route; mild operating conditions; environmentally friendly
	Sorbitol (catalytic hydrolysis + hydrogenation)	Supercritical water reforming		C: increasing the rate of hydrolysis; reducing cost of enzymatic hydrolysis; improving catalytic performance of aqueous phase reforming for sugars

[a] Energy ratio is defined as the heating value of product H_2/heating value of biomass feed. The energy ratio does not include the fossil fuel energy required for biomass production.

[b] The energy ratio value is calculated on the basis of 100% supercritical water gasification of glucose [54–56], where glucose is produced from the enzymatic hydrolysis (yield 75–95%) [159] of crystalline + amorphous cellulose (80% of dry biomass feed) [15].

and at moderate space velocities [174]. Therefore, it may not be practical to operate hydrogenation and APR reactors in series. Recently an interesting alternative was reported by Fukuoka and Dhepe whereby cellulose can be directly converted to sorbitol [189]. They showed that cellulose hydrolysis to produce glucose can be followed with glucose hydrogenation to produce sorbitol and mannitol in a single reactor. The reaction is carried out over Pt and Ru catalysts supported over γ-Al_2O_3, SiO_2–Al_2O_3 and the H form of ultrastable Y zeolite (HUSY), at temperatures ranging from 170 to 200 °C and pressure of 50 bar. The maximum yield of 31% (25% sorbitol and 6% mannitol) was obtained with Pt/γ-Al_2O_3 catalyst at 190 °C and 50 bar pressure after 24 h reaction. The authors believed that the acid sites required for the cellulose hydrolysis is produced in situ from the dissociation of H_2 over metal, in addition to the acidic sites on the support. The dissociated H_2 spills over the support site which catalyses the C–O–C bond cleavage resulting in a C=O bond and is rapidly reduced over the Pt and Ru sites to form sorbitol [189]. The resulting sorbitol can be fed to the APR reactor after a pressure reduction step to maintain the APR reactor pressure to just above the bubble point at temperatures of 200–220 °C (Fig. 10).

3. Conclusions

Hydrogen is believed to be the fuel of the future, however, there are many challenges facing the transition of liquid fuels to hydrogen. Hydrogen derived from fossil fuels will be either carbon intensive or expensive because of carbon sequestration costs. Therefore, hydrogen should be generated from resources which are carbon neutral and renewable for long term environmental sustainability. Biomass is one of the resources which can be utilised to produce hydrogen in the future. Lignocellulosic biomass is abundant and does not compete with the food resources. It is also considerably cheaper than crude oil on an energy basis. However, the existing technologies to convert lignocellulose into hydrogen are still in the nascent stages and require further development to improve the efficiency and reduce the cost of production. Table 5 illustrates the various technologies currently available and their advantages and challenges. The energy ratios of the hydrogen produced from these processes provide an insight into their inherent energy losses.

One of the most mature technologies is the biomass gasification to produce syn-gas. This technology is however very expensive due

to high energy requirements and inherent energy losses in biomass gasification [192]. Conversion of syn-gas to hydrogen by the WGS reaction is another established processes but it also suffers from energy losses [193]. The overall energy ratio (ratio of heating value of H_2 to the heating value of feed) of the conversion of biomass to hydrogen by gasification route is between 36% and 73% [21,192]. Since these technologies are already advanced from decades of research and development, it is unlikely that there will be a substantial improvement in the performance of these technologies in the coming years. Improvements in the performance can however come from new reactor designs such as catalytic membrane reactors, which enhance syn-gas conversion by shifting the equilibrium of the WGS reaction. The cost of the membranes is likely to reduce with advancements in the membrane material and production methods.

Production of bio-oils from fast pyrolysis of biomass is also a commercially available technology. Bio-oils have high oxygen and water content and are also chemically very unstable- degrading with time. Therefore, bio-oils are currently not used as fuels. Most of the bio-oils currently produced is utilised in chemicals production. Therefore, fast pyrolysis process can be optimised to produce more gases and along with the co-product strategy described in Fig. 4 these gaseous products can be separated and converted to hydrogen. The bio-oil fraction can be subsequently separated into the water-soluble and -insoluble fraction. The water-soluble fraction can be converted to hydrogen by ATR or steam reforming. Fast pyrolysis process is a cheaper technology compared to gasification [194], therefore hydrogen production costs are also be expected to cheaper. The energy ratio of hydrogen produced from fast pyrolysis is also considerably higher than gasification technology.

Finally, hydrogen can also be produced from sugars and sugar alcohols obtained from the hydrolysis of cellulose. Efficient processes are required to convert cellulosic biomass into sugar monomer. As seen from Tables 4 and 5 there are major challenges in achieving high efficiency without any environmental issues. Some of the recent catalytic routes, using metal catalysts to convert cellulose and starches into sugars and sugar alcohols are therefore promising in this regard [189,195]. APR of sugars and sugar alcohols has attracted a lot of attention recently due to its several advantages [174]. The most important advantage is that the hydrogen stream contains very low CO concentration which is ideal for fuel cell application. However, APR technology is only at the research and development stage, and Virent Energy Systems Inc. is currently working on commercialising this technology.

In future, the conversion of biomass to hydrogen will largely depend upon many regional factors. These factors include availability of excess cultivable landmass, access to suitable technologies, and political will and regulations on clean fuel. Apart from improving the performance of currently available processes, there is also a need to develop more unconventional methods for H_2 production if the hydrogen economy is to be realised in the future.

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